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PROTECTIVE COATINGS FOR CONCRETE

TECHNICAL REPORT NO. 2-29

September, 1963

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by

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U. S. ARMY ENGINEER DIVISION, OHIO RIVER

CORPS OF ENGINEERS

OHIO RIVER DIVISION LABORATORIES

CINCINNATI, OHIO

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Preface

This evaluation of the literature and bibliography covering protective coatings for portland cement concrete was begun in April, 1963 as a part of contract DA-33-017-CIVENG-63-6 between the Corps of Engineers and the Purdue Research Foundation, Purdue University. The work was performed by personnel of the School of Civil Engineering, Purdue University, K. B. Woods, Head. Source material was collected by Professor D. G. Shurig, Mr. S. J. Hanna and Mr. C. F. Scholer. Drs. W. L. Dolch and J. F. McLaughlin directed the work. Dr. Dolch prepared the final report.

Contents

Introduction

This is a review of some aspects of protective coatings for concrete. It comprises a selected bibliography with brief annotations and a summary of the state of the art as revealed by the references cited.

Since coatings for concrete is a wide-ranging subject, some restriction is necessary. Coatings are used, broadly speaking, for purposes of decoration and protection. This report is concerned exclusively with their protective function. The decorative one enters only slightly and is incidental. Coatings are used to protect a substrate from a variety of aggressive influences. Those of most importance for concrete are water penetration, chemical attack, and mechanical damage. To some extent, of course, a coating that protects against one attack protects against all. Specific materials, however, are designed for specific applications. Therefore, this report is concerned chiefly with those coatings that have been used to protect concrete from water ingress, i.e. with waterproofers and dampproofers.

Water is the chief enemy of concrete. When it freezes, the concrete may be seriously disrupted. It carries harmful solutes into and efflorescence out of the concrete. When the water content changes, the concrete shrinks and swells, and perhaps cracks, and other important properties, such as the coefficient of thermal expansion change. Frequently, its effects on the concrete aside, the penetration of water through concrete construction partially negates the purpose of the structure. Examples are wet basements and leaky dams. Such considerations determined the emphasis in this report on waterproofing coatings.

A secondary restriction is an emphasis on coatings in the usual sense of the word, that is, on those applications of comparatively small amounts of plastic substances that result in fairly thin surface treatments.

Source References Consulted

The following are the abstracting journals and bibliographies that were consulted to collect the basic list of applicable papers. The period of coverage is also given.

1. Slate, F. O., "Comprehensive Bibliography of Cement and Concrete," Eng. Expt. Sta., Purdue University, 1947, (1925-47).
2. Chemical Abstracts (1947 to date).
3. Engineering Index (1947 to date).
4. "Fifty-Five Year Index," American Concrete Institute, Detroit, (1905-59).
5. "Fifty-Year Index," (1898-1950); "Five-Year Index," (1951-55; 1956-60), American Society for Testing and Materials, Philadelphia.
6. "Publication Index," (1921-49; 1950-55; 1956-59), Highway Research Board, Washington.
7. Nuclear Science Abstracts (1948 to date).
8. Applied Science and Technology Index (Industrial Arts Index), (1947 to date).
9. Proceedings, American Concrete Institute, (1959 to date).
10. Road Abstracts, (1947 to date).

No search was made of the patent literature, *per se*, although a certain number of patents were gleaned from the above sources. The

number of patents issued for proprietary waterproofing compounds has been large, but the relative paucity of information contained in the descriptions makes them an unreliable source for objective study.

Only a few have been included in the list of references. These are those that seem to offer novel methods that have not been reported in the regular technical literature.

The large body of proprietary sales literature was sampled, but ruled out, because of the questionable claims that manufacturers advance, perhaps understandably, for their products.

Relatively few references have been included from before about 1920 since it was felt that worthwhile coating systems of that day have been further tested, usually more reliably, and reported in subsequent litarature.

Emphasis has been placed on English-language publications because of their greater availability and usefulness to the prospective readers of this review. Some of the foreign-language references have the abstract reference given with them because of its greater availability.

Basic Principles

The terms "waterproofing" and "dampproofing" are frequently used loosely. It is tempting, especially to those who sell the product, to call any treatment that reduces the penetration of water into concrete "waterproofing."

ASTM Designation: D 1079-54 (58)* defines a waterproofer as a treatment that prevents the passage of water and a dampproofer as one

*Numbers in parentheses refer to the attached bibliography.

that retards it. On this basis few coatings are waterproofers and almost anything qualifies as a dampproofer. The distinction used in this report will be that waterproofing is a treatment that is effective against the ingress of water under head and dampproofing is effective only against water absorbed by capillarity. These are, of course, hardly quantitative definitions. There have been almost no attempts to specify how much of a reduction in water ingress is enough, how high a head distinguishes "under head" from "capillarity," and so on. One can, of course, think of extreme examples. The upstream face of a dam or a wall below the water table clearly call for a "waterproofing" treatment, while vertical surfaces above grade are "dampproofing" problems. Even here the distinction is not clear-cut, since the force of wind-driven rain can vary considerably, and a treatment effective against a gentle sprinkle would not do in a storm. These matters of quantitative distinction are perhaps responsible for the confusing and contradictory state of the literature on this subject. One finds many examples of an investigator who proclaims that such and such a treatment did a good job, while another condemns it as worthless. A factor that contributes to the confusion is the tendency of most investigators to work with unspecified materials. Much of the literature refers to work with proprietary materials that are of almost unknown composition. One finds references to results with "clear sealer" or "solvent-base paint." Even when the class of substance is specified, exact information is usually lacking.

Water-resistant coatings act by one of three processes. They can render the walls of the small channels in concrete non-wetted

by water and so eliminate capillarity. They can form a continuous barrier through which only an insignificant amount of water passes by diffusion. These are the only possibilities for the elimination of the entrance of water. Silicone materials are an example of the former and bituminous membranes of the latter. The third process is to attempt only to slow down the ingress of water to an acceptable level by the imposition of a finely-pored coating on the surface. Cement-base paints are an example of this kind.

When the discrete barrier types fail, at least at first by pin-holing and cracking, the resistance to the entrance of water through these breaches is a matter of capillarity. The extent to which a grout-type of coating helps the situation involves its own capillary absorption. So in every instance the processes of capillarity are important.

When water, or any wetting liquid, forms a meniscus at the entrance to a small pore in a solid, it will be drawn into that pore by a capillary pressure that is directly proportional to the surface tension of the liquid and inversely to the radius of curvature of the meniscus. The latter is directly proportional to the size of the channel and inversely to the cosine of the wetting or contact angle. This is the angle, measured in the liquid, that the liquid-gas inter-face makes with the solid. If the pore is considered to have a circular cross-section, a commonly-used model, the expression for the capillary pressure is $2\gamma \cos\theta/r$ where γ is the liquid's surface tension, θ is the contact angle, and r is the pore radius.

If the contact angle is less than 90 degrees, the capillary pressure will bring about entrance of the liquid into the pore. The liquid is then said to wet the solid. The capillary pressure will cause ingress until it is balanced by a sufficient column of liquid, and the action will then stop at equilibrium.

If the contact angle is greater than 90 degrees the liquid is said not to wet the solid. It will then be denied entrance to the pore by the same capillary pressure that caused entrance of the wetting liquid. For a non-wetting liquid to enter such a pore it will be necessary to impose an applied external pressure to overcome the capillary pressure resistance. Mercury on glass and water on a waxed or oily surface are examples of non-wetting systems.

The rate at which a wetting liquid enters a pore is determined by a combination of the capillary pressure causing ingress and the viscous resistance to flow of the liquid in the pore at any given time. Capillary-induced flow in finely-pored systems is always viscous and no other type of flow need be considered. The orientation of the pore is seldom of importance since the capillary pressure is usually much greater than any retarding gravitational force. The capillary pressure is inversely proportional to the size of the pore; the viscous retardation is proportional to its square. Therefore, the latter factor controls the rate. That is, while the capillary potential is higher in a small pore, the rate of penetration will be greater in a large one. It is the rate that usually matters most in systems of concern in this report, since the full capillary potential is seldom realized. This is the reason that a finely-pored system

is more "water-tight" or "water-resistant" than a more coarsely-pored system, both for conditions of flow caused by capillarity and for the permeation brought about by some applied head. Incidentally, insertion of typical values in the aforementioned expression for capillary pressure shows that for concrete in many exposures the capillary pressure is greater than any hydrostatic head.

These, therefore, are the bases of the fact that water ingress into a porous system such as concrete can be eliminated or reduced to an acceptable level by increasing the wetting angle of the water on the solid, as with a silicone coating, or by reducing the pore size of the system, as with a grout or cement-base paint, as well as by interposing a discrete film or barrier.

When the details of capillary absorption are considered more closely, another important factor arises, that of specific pore geometry. If the rising meniscus comes to a region where the pore opens wider, the capillary pressure will decrease proportionately without the viscous retardation being greatly affected. The result is a decrease in the rate of absorption. This is probably a main reason for the commonly-expressed notion that air-entrained concrete is less "permeable" than non-air-entrained concrete. This is, of course, using the term "permeable", in the wrong sense. It should be restricted to the resistance to saturated flow, as determined mostly by pore size. Air-entrained concrete is more, rather than less, permeable, but its capillary absorption, or at least the rate of it, is less than that of non-air-entrained concrete.

Another such geometric factor is the influence of a constriction in the capillary pore when the wetting angle is greater than zero but less than 90 degrees. If the meniscus passes a constriction, the angle of the pore walls on the far side may be great enough to reverse the sign of the radius of meniscus curvature and bring about a cessation of liquid ingress even though the contact angle is still "wetting", i.e. less than 90 degrees. This is the so-called overturning of the meniscus and is more likely, statistically speaking, the higher the contact angle. These considerations show that contact angles measured on smooth plates in the ordinary way do not tell the whole story of capillary absorption in a porous medium.

All these questions are discussed in reviews by Adam (13, 14).

As previously implied, discrete films of materials used as protective coatings, of bitumens or polymer resins for example, have been shown to have an exceedingly small permeability and form a practically perfect seal against water. Any pinholes or cracks as a result of either weathering or imperfect application will, however, permit the entry of water. Whether water actually will enter such an imperfection is determined by the capillarity of the imperfection, but once it is passed, the capillarity of the substrate will control. The importance of the durability of a coating and its proper application is obvious. In fact, up to a certain point, the most important practical property of the materials for this type of coating is the ability to form an imperfection-free film and maintain it against the various distructive influences to which a coating is subjected. Durability is a matter subject to effective investigation. Proper

application rests on many subjective questions of motivation, inspection, and education that are most important.

It is necessary next to comment on two aspects that are not related to coatings, per se, but that are so important their omission would be a serious flaw in any picture that attempted to be reasonably complete. These are concrete quality and integral waterproofers.

There is no question that the most important single factor in the watertightness of concrete is the complex of properties that is usually understood by the term "quality." A hardened portland-cement paste of a properly low water-cement ratio and that is well-cured has been shown to have an exceedingly low permeability (19), approaching that of granites. This low permeability, in spite of a porosity of at least 25 percent and in any practical instance more, is the result of the smallness of the pores in such a paste. At higher water-cement ratios, however, not only is there an increasing proportion of relatively large pores, but they begin to hook up into an interconnected network, and the permeability of the paste increases rapidly (20).

When a well-graded aggregate is dispersed throughout a high-quality paste and the mass is properly consolidated in the forms to eliminate honey-combing voids, properly finished to eliminate bleeding channels, and properly cured to permit adequate development of the hydration product the resulting concrete is so impermeable that any waterproofing coating would be superfluous. If, in addition, a suitable amount of properly-entrained air (16) is incorporated in the concrete, it will be, for any ordinary purpose, completely impervious

to water invasion and destructive action caused thereby. The dependence of the properties of concrete on the quality of the paste has been reviewed by Powers (18).

Many investigators and agencies (see ref. 11 for one example) place reliance for watertightness in all ordinary exposures on the production of such a high-quality concrete. In these circumstances any waterproofer is probably only an "insurance policy" against poor workmanship or bad luck.

These are the reasons that one sees listed as "waterproofers", substances that have no water-repellent action, but serve rather to insure the attainment of high-quality concrete. Prominent among these are air-entraining agents, water reducers, and accelerators.

Air-entraining agents not only do their primary job with respect to the frost-protection of the hardened concrete, but they also result in a less-absorptive concrete by the mechanism previously mentioned. In addition, they frequently permit a reduction in the water content and an increased workability. This means a dryer and more homogeneous concrete and one that bleeds less.

Water-reducers, as their name implies, permit a decreased water-content of the concrete at constant workability and result in the benefits of less mix water, including lower permeability and higher strength (15).

Accelerators, of which calcium chloride is the best-known example, speed up the hydration and give a dense structure more rapidly and are therefore "waterproofers" in a loose sense of the word.

Any additive or construction measure that results in a higher-quality concrete will benefit its watertightness and perhaps obviate the need for any special coating. Chief among these are probably air-entrainment, restraint at the water valve, and good inspection. All these questions of concrete quality apply, of course, only to new construction.

Integral waterproofers are substances that are incorporated in the mixture to render the hardened concrete less absorptive (29, 33). They should probably not be called waterproofers at all, but are, by the above definitions, only dampproofers at best. A variety of substances has been used, but most fall into two classes - finely-divided pore-filling materials or insoluble-soaps that supposedly impart hydrophobic qualities to the concrete (32, 34). The finely divided materials increase the water-demand and therefore, to some extent, offset their own purpose. An increase in the cement content probably is more effective (34a). Most investigators have found little benefit from integral waterproofers (25, 27, 34a). Frequently the permeability of the concrete increased and its strength decreased, although some relatively short-time reduction in capillary absorption was often obtained. The general conclusion seems to be that integral waterproofers are not dependable to effect any important reduction in water penetration of concrete so-treated.

Types of Coatings

Because of the common occurrence of blends of various types of materials it is difficult to categorize concrete coatings,

unambiguously but in general they fall into the following classes and will be discussed in these groups.

1. Cement-base paints
2. Solvent-thinned paints
3. Emulsion paints
4. Bituminous coatings
5. Silicones
6. Epoxy and related coatings
7. Miscellaneous coatings

Several reviews of the general subject of waterproof coatings have been published. The Bureau of Reclamation Paint Manual (11) is reasonably comprehensive and has been revised from time to time. The book edited by Moilliet (6) is recent, although the chapter by Michaels (5) deals more with soils than concrete. Hunter's book (64) places particular, but not exclusive, emphasis on bituminous materials, and gives many drawings showing construction details that are important to some waterproofing applications. Lea's review (4) is brief but complete for the older methods. One of the best short reviews found in the search is that by Allyn (1).

Surface Preparation

Some aspects of the preparation of the surface to receive a water-resistant coating are common to most coating types and will be mentioned here. The question is discussed in several reviews, particularly (1, 7, 11, 37). Specific points will be taken up in connection with specific coatings.

In general, the concrete surface to which a coating will be applied should be clean, sound, and dense enough to provide a good base for the coating.

Dirt should be brushed off or hosed off. Organic material, such as oil drippings from automobiles, may have to be removed with

a strong detergent. Form oil or curing compounds can be allowed to weather for several months or sand blasted.

A sound base should be provided. Sand blasting is one of the best methods. Rubbing with a coarse-grit abrasive stone is another. Laitance should be removed and can be etched away, especially on horizontal surfaces, with a solution of about 10 percent hydrochloric acid, which then must be flushed off completely.

For some coatings, such as asphalt membranes, small irregularities in the surface may matter little. For those situations where appearance is important, as good a surface as possible should be provided. Holes and cracks should be filled and repaired by the usual methods. Relatively small irregularities can be smoothed by brushing in a cement-sand grout. In these instances, such as some concrete block, where the surface is too rough for proper application of some coatings, an initial coverage with a cement-base paint, worked in well, will provide a proper base for subsequent coats.

In general, coatings that have an organic solvent base cannot be applied to wet concrete, while water-base materials, emulsions or solutions, can. This represents a distinct advantage of water-base coatings in many instances.

Cement-Base Paints

A cement-base paint is a mixture of portland cement and a lesser amount of slaked lime that is mixed with enough water just prior to its application to make a paint of a fairly thick consistency. Usually there are also incorporated relatively small amounts of pigment, calcium chloride to accelerate set, and a water repellent

compound such as a stearate. Sometime a silicious filler is added. For thicker application into a coarse surface a fine sand can be added to make a quasi-grout.

The paint is brushed well into a wetted surface that has aged at least a month subsequent to being poured.

The nature and use of cement-base paints is covered in a recommended practice of the American Concrete Institute (35).

If an emulsion base material, such as casein, is substituted for part of the mixing water a so-called fill coat is obtained that is slower to dry out, more flexible, and has better adhesion than straight cement-base paints.

All paints with a cement base should be water-cured to allow as complete as possible a hydration of the cement. These paints form a film that is continuous, but, of course, is inherently porous. They can, therefore, be put only in the category of damp-proofers.

The relatively limited research on these materials has shown that they are comparatively inefficient as water barriers. One could hardly expect otherwise. They are used more frequently on interior than exterior surfaces. Investigators (22, 36) have, however, shown comparatively large variations in performance. Some cement-base paints seem to be considerably better than others, but none has been found to be particularly good at keeping out water.

These paints are durable and allow the surface to "breathe." They are, therefore, not broken loose by vapor pressure behind them as are some denser coatings. This is another reason for their use

on interior walls where a certain amount of vapor permeability is desirable. If the surface to which they are applied is too smooth, these paints can fail by flaking and loss of bond. The alkalis in cement do not, of course, influence them adversely.

Somewhat in the same category as cement-base paints are the thicker coatings that result from the application of a grout to a surface. It may be that such coatings are thick enough to do more good than the thinner cement paint. Washa (28) for example found a 1:1 grout to be the most efficient in reducing the permeability of a concrete sample of all the coatings he tested. Unfortunately, as is so often the case, important details, such as the thickness of the grout coating and its water-cement ratio, are lacking. The great importance of adequate curing of such coatings was emphasized.

Mention of straight grouts as water resistant coatings is absent from the recent literature. It is probably difficult to obtain proper adhesion and curing and the absence of cracks that would destroy the coating's usefulness. Modified grouts, i.e. latex-modified mortars, are a recent development and will be discussed in another section.

Solvent-Thinned Paints

This class of coatings is a large one, and the title of the section is perhaps misleading because it includes many types of materials that are frequently described as varnishes, lacquers, and solutions. The class includes all coatings that have a volatile solvent other than water as a part or all of their vehicle.

Exceptions are such materials as bituminous cutbacks that are treated in other sections. Included also here is straight linseed oil, that can be, but is not always, solvent-thinned.

This class of coatings is treated extensively in the general references (1, 11, 23, 25, 26, 39) and forms the main subject of the American Concrete Institute's recommended practice (37).

The oil-base paints, used so extensively on exterior wood, form a large group. They are composed essentially of a pigment suspended in a vehicle that contains a volatile solvent and a nonvolatile drying oil that cures by oxidation and polymerization to become the binder of the coating. Linseed oil is by far the most-used drying oil. Small amounts of special purpose materials are frequently included, which is, indeed, true of almost all the coatings described in this section. The number of individual formulations is so large that only generalities can be considered here.

One of the difficulties with oil-base paints is their susceptibility to the saponifying influence of the alkalis always present in concrete. This action can ruin the film. The usual way to deal with the problem is to allow the surface to weather for six months or so and reduce the alkalinity of the exterior of the concrete by carbonation. Of the various pre-treatments that have been tried in order to shorten this period prior to painting, one of the most effective in laboratory tests has been a solution of zinc chloride and phosphoric acid (40). Seasoning is said to be a more reliable recourse, however, than the chemical pretreatment (37).

Paints marketed for use on masonry usually have additives to improve their alkali resistance. For these paints the six-month seasoning period can be reduced to perhaps two. These paints, like all solvent-base coatings, cannot be applied to wet concrete. The surface, at least, must be dry, and the deeper the dryness goes the better.

Oil-base paints, when properly applied, are durable (39), and form a good water-resistant coating. They are not intended for use under a head of water, nor where subjected to constant dampness. They are generally thought of as dampproofers rather than waterproofers, although Blackburn (23) found them to be better than many other types of coatings in an immersion test.

These paints, in common with most other relatively thin continuous coatings, can easily fail by blistering, loss of bond, and peeling when subjected to the condition of moisture in the concrete behind them. Generally speaking, all such films are of little use when the moisture comes through the concrete to the coating.

Oil-base paints are formulated to weather by chalking, and they form a good base for repainting.

Closely-allied to the oil-base paints is the straight linseed oil coating. This material is, of course, unpigmented and may suffer thereby, since one of the functions of a pigment is to protect the binder from the harmful effects of light.

Linseed oil, either alone or followed by an oil-base paint has been used as a surface treatment of concrete for many years (44, 45). It seems, as of this writing, to be undergoing a revival of favor (41, 46).

Klieger and Perenchio (73) found straight linseed oil to be a better treatment than many of the silicones they tested.

If a natural or synthetic resin is incorporated in the vehicle, a varnish-base paint is obtained. Here again the terminology is inexact. Some call the vehicle of any paint a "varnish." Others refer to a solution of a resin as a "varnish," especially if the solvent is not as fast-drying as that of a "lacquer." Since the question permits a certain latitude, in this report the terminology of Carman (3) will be used, and the term "varnish' will refer only to a material that has a vehicle containing both a resin and a drying oil. An "enamel" is a pigmented varnish. A "lacquer" is a solution of a resin in a volatile solvent, from which the resin is usually deposited on the surface unchanged, although it may be polymerized further by appropriate means after its deposition.

The alkyds are the synthetic resins probably most commonly-used in varnishes, and they seem to be rapidly replacing the natural resins. Varnishes and enamels are better leveling than oil-base paints, dry more rapidly to a smoother finish of controlled gloss, and result in a harder film. There is little information comparing their performance as dampproofers with that of oil-base paints. Probably the two are about equal. The general use of varnishes and enamels for interior coatings and oil-base paints for exteriors (37) may be based on their different weathering characteristics. Those varnishes specifically formulated for exterior use, such as spar, are of the so-called long-oil type, i.e. with a vehicle containing a relatively large amount of drying oil that results in a more flexible film.

Lacquers, as defined above, can be a solution of almost any resin in almost any solvent. Sometimes the use of the word is restricted to a certain resin, e.g. nitrocellulose, but here it will be used in a general sense.

The resins that seem to have been applied most successfully as lacquers to concrete have been the rubber-like materials, vinyls, urethanes, and epoxies. Since these lacquers have no drying oils in their formulations they are, in contrast to the oil-base or varnish-base paints, resistant to the saponifying influences of the alkalis in concrete. Therefore, aging or chemical pretreatment of the surface are not necessary prior to their application, and they can be used under conditions of dampness that would destroy the oil-containing types.

The "synthetic rubbers" used as coatings include chlorinated-rubber, styrene-butadiene copolymers, and neoprene.

Chlorinated rubber is used as a heavy-duty coating for concrete (47), and is blended with varnish-type coatings (43) to improve their properties. It has excellent adhesion and forms a coating strongly resistant to water and many chemicals. Its susceptibility to sunlight can be improved with epoxy stabilizers, and its inherent brittleness overcome with plasticizers (9). Chlorinated-rubber is also frequently used as a first, prime coat for subsequent applications of neoprene or vinyl that otherwise have poor adhesion to concrete (9).

Neoprene, or polychloroprene, is used as a very heavy duty coating material. It requires a chlorinated-rubber primer, and is usually used in thicker layers - around 20 mils - than the usual solvent-base coating. Neoprene coatings have many industrial applications in the metal-protecting field (9). They have also been

used to coat the upstream faces of dams (11), and have the elasticity to bridge small cracks in the concrete. This last is an important, even crucial factor in the relatively thick coatings that are used as waterproofers to impermeabilize a substrate. The subject is discussed further in connection with bituminous membranes. Neoprene coatings also have been useful where cavitation is a problem.

Styrene-butadiene copolymers are similar to Buna-S rubber except there is a greater proportion of styrene in the former. These coatings have good adhesion and fair durability. This resin is also the base of a large group of water-thinned paints.

Another very resistant type of coating is the vinyl. At present the most commonly-used resin in the vinyl coating class is a vinyl chloride-vinyl acetate copolymer (9). Coatings of this material are extremely resistant to corrosive chemicals and can be used satisfactorily in situations where they are continuously or frequently wet, such as in showers (37). Vinyls do not adhere well to unprimed concrete; frequently a chlorinated-rubber prime coat is used.

Epoxy and urethane coatings can be applied either as an unmodified, total-resin coating or as a solvent-thinned lacquer. They give films that are strong and durable. The article by Mason (89) describes the use of urethane floor coatings. They are very abrasion-resistant and unusually flexible for such a resistant coating. The epoxy coatings, unless modified, are relatively brittle, but strong. Their adhesion to many substrates is excellent.

There is little data on the use of epoxy or polyurethane paints as water-resistant coatings. Presumably they are superior

to many other solvent-thinned coatings. Both these materials are relatively new. Further experience will be needed to evaluate their potential as concrete coatings. Straight epoxy coatings are discussed in another section.

Another group of coatings that fall in the general class of solvent-thinned paints is that frequently called "clear coatings" or "sealers" or "solutions." These are solutions of waxes or oils, with sometimes small amounts of silicones or soaps added for their water-repellency effect. These materials are useful as dampproofers, especially where an unpigmented material is needed so as not to change the appearance of the surface. They are probably not as good as a regular paint nor as durable because they lack the protective action of the pigment.

Other resins than those mentioned above have been used as lacquer-base coatings. Acrylics, vinylidenses, and chlorosulfonated polyethylene have been used, but no explicit mention of their use on concrete was found.

It should be emphasized again that, up to a certain limit that depends on the type of material, the success of any coating of the continuous film type is dependent on all those matters of surface preparation, application, and durability that guarantee as imperfection-free a film as possible. Far more water comes through cracks and pinholes, to say nothing of broken blisters, other large ruptures, and areas that never got coated to begin with, than comes through an intact coating. The main reason for the application of more than one coat of any of these materials is not so much to

increase the thickness of the coating as to insure freedom from defects. An important advantage to relatively thick coatings is their greater mechanical strength that helps maintain an intact barrier against the destructive processes that assail a coating.

Emulsion Paints

A comparatively recent development has been the use of water-thinned emulsion paints as exterior protective coatings for concrete (1, 50, 54). These paints are emulsions of a resin in water, among with pigments and the small amounts of dispersing agents that stabilize the emulsion. These materials are frequently called latex paints because of their similarity to natural latex, an emulsion of rubber hydrocarbons. For the same reason they are also loosely called rubber-base paints, whether or not the dispersed resin in the vehicle is an elastomer similar to rubber.

Emulsion paints have become popular in a short time because of their many practical advantages. They are simple to apply, relatively odorless, dry very quickly, can be recoated soon, and can be washed from the tools easily with only water. For use on concrete they have the added advantages that they are alkali resistant, so no special aging or pretreatment is necessary, and they can be applied satisfactorily to damp surfaces.

The early formulations of these paints were for interior application and their wide acceptance has been based largely on such use. More recently, however, they have been made suitable for exterior use.

The earliest latexes were those using styrene-butadiene resins (54). These paints have good adherence and alkali-resistance, but are slower than some others to develop their resistance to moisture (1). Polyvinyl acetate emulsions dry faster and are as good in other respects. The third resin type most used in emulsion paints is acrylic, and these dry even faster. They also are reported to give films of excellent flexibility and durability (50).

These paints are so recent a development that definite statements about their water resistance are not yet possible. Seymour and Steiner (9) state that many resin emulsion coatings are more water absorbent and permeable than are comparable films deposited from solvent-base lacquers. The reason is presumably that the non-volatile emulsifiers stay in the film and are hydrophilic. Emulsion paints will, therefore, have a relatively high water-vapor permeability and "breathe" well. This property is sometimes an advantage.

In spite of perhaps a poorer water resistance than their solvent-base counterparts, the emulsion paints may be more practical for many purposes because of their ease of application.

Other resins than those mentioned above have been used with success (51, 5[illegible]). Some years ago Tuthill (55) reported the successful coating of holds in concrete ships with a Thiokol emulsion reinforced with Osnaberg fabric. Paraffin emulsions have also been used in water-resistant formulations for use on concrete (53).

Bituminous Coatings

Coatings of bituminous materials are probably the oldest (Gen. 6:14) and most widely-used waterproofing coatings. Until

the advent of relatively new materials, a thick bituminous coating was probably the only one that deserved the name of waterproofer, literally interpreted. These materials are so important that standard specifications for them have been developed for many years (58).

Bituminous coatings can be composed of either asphalt or tar for the bituminous material, and can vary from relatively thin applications of a cutback or emulsion through moppings of pitches and asphalt cements to grouts, mastics, and built-up membranes.

In most of the early work on water resistant coatings, in which usually a large variety of materials was tested and compared, invariably a conclusion was that bituminous materials were among the best (25, 28, 64, 66, 67). This experience has been so universal that to some extent even now the term "waterproofing" is synonymous with bituminous materials.

Careful measurement of the diffusion of water through intact bituminous films (59) has shown the amount to be negligible. For all practical purposes one can say that such a film is completely impermeable to water. The essence of the problem then, as has been stated in connection with other types of coatings, is to adopt materials and practices that insure the establishment and retention of an intact film. This requirement involves special considerations with bituminous materials.

The lighter coats, of cutbacks or emulsions, are advocated for dampproofing exposure only, that is for relatively less severe conditions. These are applied by spray or brush. The surface must

be dry for cutbacks, but can be damp for the application of emulsions. They are frequently fortified with fillers of some kind to permit the build up of a thicker coating, more stable to disruptive influences. Blackburn (61) tested a large variety of kinds of relatively thin bituminous coatings, and found asphalt cut-backs with asbestos fiber fillers to give particularly effective coatings. He also found the emulsions he used were, as a class, less water resistant than the other types, but those emulsions stabilized by clay were superior to those stabilized by soap. A possible reason for this finding is the greater thicknesses that can be applied of a clay-type, as opposed to a soap-type, emulsion, and the resulting "honey comb" type of structure that has an appreciable mechanical and heat stability.

A common practice is to mop on a coat of the heated asphalt cement or coal tar pitch alone. This results in thicker coatings, say 20-50 mils, but because of the rheological and weathering characteristics of these substances these coatings may not necessarily be more stable than thinner applications (61).

Bituminous materials are generally divided into classes for different waterproofing uses. There are three classes of asphalts and two of coal tar pitch specified by ASTM (58). The softer, lower melting, and more ductile materials are recommended for below ground use while the harder ones are for above ground application where they may have to rest on inclined surfaces without the stabilizing effects of any backfill.

It is considered good practice to prime the surface to which a relatively thick bituminous application will be made. A material

is used that will penetrate farther into the surface than will bituminous materials themselves. These prime coats are usually cutbacks of some sort for asphalt coatings and creosote for coal tar pitches. There are also standard specifications for these materials (58).

Thicker and more stable films can be built up by the use of grouts, mastics, and membranes. A grout or mastic contains aggregate in addition to the bituminous binder. A grout is roughly half binder and the aggregate size is small. A mastic contains sand size aggregate and only 12 percent or so of binder (58). Mechanically the distinction between the two is that grouts will flow naturally into place while mastics must be manipulated, by trowelling for instance. Grouts are frequently used to protect membranes from damage. Mastics are widely used as relatively heavy-duty waterproofing coatings.

The heaviest duty bituminous coating is a membrane formed by moppings of asphalt or tar into which are layed two to five layers of some kind of bituminous-impregnated fabric as a stabilizer. The commonest fabrics, for which there are ASTM specifications (58), are burlap, cotton fabric, woven glass, and felts. A properly-constructed, intact bituminous membrane is probably the best waterproofing coating presently available, in spite of the attractions of neoprenes, epoxies, and the like.

Bituminous materials have certain properties that may make the obtaining of a durable intact coating difficult. One of these properties is their temperature sensitivity. They have desirable

rheological properties over a comparatively limited temperature range. At higher temperatures they flow too readily and at lower ones, unfortunately those commonly encountered, the ductility of bitumens is so reduced that they crack easily. A waterproofing coating should have the ability to deform and remain intact when small cracks occur in the substrate due to applied loads or volume changes. It should be able to bridge cracks without rupturing. Some of the newer coatings, such as neoprene, may be superior to bituminous materials in these respects.

An interesting investigation was made of the durability of bituminous membranes (64) to determine their extensibility prior to cracking at various low temperatures. Only the above-ground type of asphalts were found to be satisfactory, especially with cotton fabric.

Bitumens are also subject to deterioration by oxidation and other chemical processes under the action of air and sunlight (63). These changes can lead to embrittlement of the film and consequent cracking. Underground bituminous materials can be attacked by bacterial action.

A straight asphalt cement or coal tar pitch or mastics containing them must be heated to be applied to a substrate. This heating can, if excessive, alter the composition of the material so that the resulting film is too brittle and, therefore, less durable. Overheating is apparently a common fault in the application of these substances. A further difficulty with the application of hot material is that any air trapped under the coating in a void of the surface

will expand under the heat and deform the still soft bitumen. This action results in either a pinhole or a blister that will break easily.

All such factors must be considered when these materials are used. Care in back-filling, caution against overheating, the construction of a protective layer of grout or portland cement concrete over the waterproofing, and so on, are frequently called for in an effort to insure an intact and durable coating.

Questions of durability seem to be especially important in the straight mopping type of coating. In outdoor and accelerated weathering tests of asphalts and coal tar pitches of all major types Blackburn (61) found most of the materials either flowed off an inclined surface or developed cracks that would be disastrous to any waterproofing function. He also showed the great importance of freedom from pinholes.

The coal tar pitches are especially temperature sensitive (11). They sag and run at higher temperatures and become brittle at lower ones to a greater extent than do asphalt cements. The pitches are consequently frequently restricted to underground applications where they will be undisturbed and subject to only small temperature variations.

Some improvement can be made by incorporating fillers and by other processing to produce a so-called coal-tar enamel. This material, however, demands great care in its application.

In spite of the low cost of bituminous materials, these important matters of durability and care in application have

caused misgivings about their use and a search for better, even though costlier, materials.

Silicone Treatments

A silicone treatment of concrete is designed to deposit a water-repellent film on the pore walls of the substrate so that a high contact angle will exist with water, which will, therefore, be denied entrance by the capillary pressure previously mentioned.

Since a continuous coating is not formed, a silicone treatment permits the concrete to "breathe," that is, it can lose or gain water vapor. The same capillary pressure that denies entrance to water prevents the exit of salt-bearing solutions from the interior and, therefore, prevents the efflorescence common to many masonry structures.

Other subsidiary benefits are also claimed, for example that since treated surfaces are water repellent they do not darken so readily when subject to rain (72). Highway structures and pavements, therefore, are said to be more light-reflecting when treated.

Two basic types of materials are used in silicone treatments of concrete. These are generally distinguished as "solvent-base" or "water-base" silicones.

The solvent-base type is a silicone resin that contains reactive groups and is soluble in organic solvents (5, 70). A solution containing about 5 percent silicone solids is sprayed, or otherwise flooded on the concrete surface, which must be dry. The solution penetrates a short distance into the concrete, and the

solvent evaporates. The residual silicone resin is bonded by chemical bonds (5) to the substrate and presents a hydrocarbon-group surface that has a high contact angle with water and prevents capillary attraction.

There are differences in composition of the resins produced by various companies for this purpose. Patents for particular formulations have been issued. Bass and Porter (70) give examples of especially effective compositions.

The water-base type is a solution of an alkali salt of a siliconic acid. That most frequently-used is sodium methyl siliconate (5, 70, 78), although others have been tried (83). This solution is highly alkaline by hydrolysis. The alkalinity is a hazard associated with the use of this type, just as flammability of the solvent is with the other type. Users seem generally to prefer the fire hazard to the alkalinity.

A water solution penetrates and dries and the residual silicone reacts with moisture and atmospheric carbon dioxide to yield a cross-linked polymer bonded to the substrate (70). This film presents a hydrocarbon-group surface that has a large contact angle with water and is similar to that deposited from the solvent-base products. An important difference between the two types is that the water-base silicone can be applied to a damp surface, while the solvent-type cannot.

Silicones of either type are used, of course, only as dampproofers in the sense that the distinction is made here. The head of water needed to overcome their capillary repellency is not large, and they are not designed to withstand such conditions.

When silicones first appeared, they were hailed as the solution to certain highway problems. It was hoped they could be used to reduce damage to pavements and structures and, in particular, to reduce the scaling and deterioration of bridges caused by freezing and thawing and greatly accelerated by the increasing application of de-icing salts.

Many field tests of these materials have been made, some of which have been incidental to ordinary highway maintenance and the results of which, therefore, do not appear in the literature. Several laboratory investigations have been performed to evaluate silicones under more controlled conditions (72, 76, 77, 78, 79, 81, 82).

The results of all this work have been conflicting, and opinion is still divided. In general, however, it is safe to say the results of highway applications have been disappointing and these materials have not fulfilled the hopes that were once held for them.

Some workers have reported distinct advantages, including lessened absorption and scaling of treated concrete (71, 72, 81, 82). Others have qualified their approval, stating that non-air-entrained concrete was helped but air-entrained was not (76), the materials were ineffective on lightweight, porous concrete (81), and water-base materials were effective on limestone, but solvent-base types were not (80).

Still other tests, field and laboratory, have shown no benefit at all (77), and some recently-reported work (79) has resulted in the conclusion that these materials can even be harmful, concrete

so-treated having poorer durability in some instances than untreated specimens.

It is difficult to resolve the differences that various workers have found, particularly in laboratory studies. Seemingly small differences in immersion head, for instance, might make relatively large differences in the water absorption and, therefore, the durability obtained. Breakdown or destruction of the silicone film itself may have influenced the results. Most workers agree that freshly-treated concrete is less absorbent by capillary action than untreated concrete. But the repellent effect seems to disappear with age. This may be due to the action of light and air. Tests of silicone films on glass plates (73) exposed to accelerated weathering have shown a considerable decrease in the wetting angle to water. It might, however, be argued that the silicone film deposited below the surface of the concrete would be protected from destruction by weathering. Manufacturers have generally claimed 3 to 5 years of effective life for their treatments.

Another factor tending to confuse some field results is that comparison is made with an untreated, but air-entrained, section that would be expected to show little frost damage anyway. The statement, then, that the silicone was no improvement does not mean much. On the other hand, silicone-treated sections have been observed to deteriorate in certain respects, for instance in susceptibility to pop-outs, just as rapidly as untreated sections (74).

One gets the impression, difficult to document (see Fig. 2 of Allyn, ref. 1, for one example) but reasonable, that experience with silicones has been more satisfactory on vertical than on horizontal surfaces.

In recent years variations in the uses of these materials have been made. Silicones have been incorporated with other coating materials, for instance a rubber latex (51), to give a combined effect. They have also been promoted as integral materials for concrete mixtures. Recent tests reported by Grieb (75) show such use to result in improvement of important properties of the concrete tested, although a serious set retardation occurred also. This type of usage is presently an expensive one.

Epoxy and Related Coatings

This section is a description of some coatings that are formed in situ by a reaction after the coating has been deposited on the substrate. Oil-base paint coatings are an example, since the oxidation of the drying oil is such a polymerization reaction, but these types have been considered elsewhere.

There may be advantages to the use of a non-solvent type of coating for the laying down of a resin film. If the film is a resin coating formed by simple deposition from solution, the evaporation of the solvent may disturb the film-formation process and result in pinholes or other undesirable conditions of the final film. Such defects will not occur in those coatings where there is no solvent, or at least not much, and all of the applied material forms the final coating after the appropriate chemical changes have taken place.

The most important class of materials in this category is the epoxy resins. Epoxy resins are used in a wide variety of applications, and in the concrete field they are used in many ways besides coatings. They have been successfully used as bonding and patching materials, as anti-skid applications, and as binders in grouts, mortars, and concretes. Although relatively new in the construction field, these resins have become important and are the subject of books and reviews (87, 88, 92, 93). The American Concrete Institute has recently published a guide (84) to the use of epoxy materials that covers all aspects of their use with concrete.

Epoxy resins are usually generated from epichlorohydrin and bisphenol-A. They are then mixed on the job with a second component containing a curing agent that brings about cross-linking and further polymerization. Various pigments, fillers, extenders and diluents are also frequently included, sometimes to obtain special desired properties and also to reduce the cost.

The mixture is applied to the concrete surface in appropriate ways. In a relatively short time, longer at lower temperatures, the material sets to a hard resin that has excellent bond.

Especially important is the preparation of the surface. It must be sound, clean, and dry. Laitance and other unsound material can be removed by sand blasting, grinding, acid-etching, and the like. Oily deposits, as on pavements, can be removed with strong detergents, or solvents. Some failures of epoxy materials have been traced to inadequate surface preparation. The ACI guide (84) gives a proposed test method to determine the adequacy of the surface preparation in which the force needed to detach a pipe cap that has been bonded to the surface is measured.

The hardened epoxy coat is exceedingly strong, stronger usually than the concrete to which it is bonded so that mechanical failures occur in the concrete, not at the epoxy-to-surface bond. The film is also resistant to water and many chemicals, and forms a heavy-duty waterproofing coating. These materials are durable, and field tests show them to deteriorate more frequently by bond breaking and flaking off than by weathering of the coating itself.

One defect with these materials for some applications is their great rigidity, and another is their coefficient of thermal expansion that is considerably different from that of concrete. This has resulted in disruption of some coatings and other applications under relatively large temperature variations. An apparently successful measure to combat this defect is the extension of the epoxy with a bituminous material to improve its flexibility as well as lower the cost.

Other difficulties are the temperature susceptibility of the reaction that may necessitate artificial heating in some instances, the mild skin irritation caused by these materials in some individuals, and the necessity to clean tools immediately after use with special solvents.

There are few reports of the use of epoxy coatings specifically as waterproofers, but there is every indication that such use will become more frequent because of their many almost ideal properties and because of the probable cost reduction. These resins are also the base of solvent-thinned lacquers, the use of which is also increasing. Frequently too, they serve a waterproofing function

in addition or incidental to their other uses, such as skid-resistant overlays.

Mason (89) described a two-component polyurethane coating used as a concrete floor coating. This material was reported to have outstanding wear resistance and flexibility. No explicit mention of the use of urethane coatings as concrete waterproofers was found, but their properties as floor paints and their increasing use as a varnish base imply good water retarding properties.

Miscellaneous Coatings

In this section are lumped a variety of coatings that seem more appropriately consolidated, rather than having a large number of special categories.

As stated at the outset, this review is restricted to coatings in more or less the ordinary sense of the word. Relatively thick applications of material that have structural significance in themselves, such as pavement overlays for example, have been excluded, although they obviously also serve a protective and water-resistant function. But their action is obvious. There is, however, one such system that has enough exceptional features to warrant mention. This is the relatively thin surface treatment of a mortar containing a resin latex admixture. Certain latexes, when incorporated in relatively large amounts (10-20 percent of the cement) in a cement mortar or mastic confer unusual properties on the resulting hardened mass. Such mortars have increased flexural strength, decreased absorption, and greater resistance to chemical attack (94, 95). They can be applied in thicknesses of only a fraction

of an inch and will bond well to underlying concrete, dry and harden without cracking, and result in a satisfactory surfacing treatment that confers an appreciable watertightness to the underlying substrate. Applications have been made satisfactorily to repair scaled bridge decks, for example. Such "coatings" are not inexpensive, and would probably not be a first choice for the ordinary waterproofing problem, although for special applications they have a place.

Water resistant coatings can be formed by application of a molten or semi-molten resin to the concrete surface. Bituminous cements and pitches are examples already covered. Sometimes it is necessary to use this method because no solvent is possible in which to dissolve the coating material. Polyethylene is an example. Coatings of it have been applied with the flame-spray technique, although it is stated to yield films subject to pinholes and imperfections that can be lessened by blending the polyethylene with polyisobutylene (9). Thiokol rubbers have also been applied with the flame-spray method (9) and have been found to have good cavitation resistance (11). A Japanese patent has also been issued for a polyethylene-in-oil gel for waterproofing concrete (97).

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50. Allyn, G., "Acrylic Resin Emulsion Paints for Masonry," Eng. Progress at Univ. of Florida 11, Dec. 1957.

A review of laboratory and field application of acrylic resin emulsion paints on exterior masonry. They give good resistance to moisture, alkali, blistering, and mildew, and are durable.

51. Hurst, H., Civil Eng. and Public Works Rev. 57, 1175 (1962).

An account of a method of wall treatment that uses a mixture of a water-base silicone and a natural rubber latex.

52. Mitchell, W. S., "Effect of a Waterproof Coating on Concrete Durability," J. Am. Concrete Inst. 29, 51 (1957).

A discussion of the destructive role of water in concrete. Some experimental work is cited showing high resistance of Neoprene latex-coated specimens when subjected to freezing and thawing.

53. Mori, S. and Matsuda, O., "Waterproofing Agent Containing Paraffin for Concrete," Semento Gijutsu Nempo 13, 277 (1959); C.A. 55, 16949.

Paraffin was emulsified using a non-ionic surfactant and was added to a finely-divided silica powder. This mixture decreased the water absorption and permeability of concrete blocks and increased their strength.

54. Quigley, F. K. Jr., "Styrene-Butadiene Latexes for Exterior Masonry Paints," Eng. Progress at Univ. of Florida 11, Dec. 1957.

A review of the qualities of styrene-butadiene latexes as exterior paints. They are durable, inexpensive, and alkali-resistant.

55. Tuthill, L. H., "Concrete Operations in the Concrete Ship Program," Proc. Am. Concrete Inst. 41, 137 (1945).

Reports the use of a Thiokol emulsion on the holds of concrete ships. The coating was reinforced with Osnaberg fabric.

56. Wise, J. K., ed., "Emulsion Paints, A Symposium," Ind. Eng. Chem. 45, 709 (1953).

A general discussion of particular interest is the paper by Brown and Scullin on "Water Penetration of Emulsion Polymer Films," which discusses the mechanism. It is stated to be a diffusion process that does not involve capillarity and is dependent on the elasticity of the film.

Bituminous Coatings

57. Abraham, H., "Asphalts and Allied Substances," 6th ed. (5 volumes), D. Van Nostrand Co., Princeton, N. J., 1962.

A general reference to all aspects of asphalts.

58. American Society for Testing and Materials, "ASTM Standards 1961, Part 4," Philadelphia.

Specifications and test methods covering all bituminous and accessory materials, such as fabric and felts, for use in waterproofing and dampproofing.

59. Anderson, A. P. and Wright, K. A., "Permeability and Absorption Properties of Bituminous Coatings," Ind. Eng. Chem. 33, 991 (1941).

Laboratory experiments showed that the penetration of an intact bituminous film by water is negligible.

60. AREA Committee 29 on Waterproofing, "The Ability of Various Waterproofing Membranes to Bridge Cracks that Might Develop in Concrete on Which They are Applied," Proc. Am. Railway Eng. Assoc. 62, 153 (1961).

A test method was devised to determine the ability of a waterproofing membrane to deform and maintain watertightness. This test was applied to many combinations of fabrics, felts, tars, and asphalts. Below about 40F only the above-ground asphalt was appreciably extensible. Cotton fabric was better than felt. Three-ply cotton fabric membranes were better than 2-ply, 3-ply felt, or 5-ply combinations. No. 400 roofing canvas was a good membrane-forming material.

61. Blackburn, J. B., "A Study of Bituminous Waterproofing Coatings," Proc. Am. Railway Eng. Assoc. 58, 293 (1957).

A field and laboratory study using asphalt cements, coal-tar pitches, asphalt cutbacks and emulsions, and coal-tar emulsions. The cements and pitches were effective waterproofers, but the pitches were more susceptible to temperature changes, giving excessive flow or brittleness. The asphalt cut-backs with asbestos fiber fillers were good materials. Clay-type emulsions were superior to soap-type, but the emulsions as a class were not as good as the other materials on long immersion.

62. Duriez, M., "Mortars and Concretes Having a Plastic Binder Base as Used in Road Construction and Waterproofing," Ann. Inst. Batiment 8, 553 (1955); Hwy. Res. Abs., April 1956.

A general article on bituminous concrete and mortars including their use as waterproofing coatings on dams and canal walls.

63. HRB Committee on Resistance of Bituminous Materials, "Bibliography on Resistance of Bituminous Materials to Deterioration Caused by Physical and Chemical Changes," Highway Res. Board Bibliog. No. 9, 89 pp. (1951).

An annotated bibliography on all aspects of deterioration of bituminous materials.

64. Hunter, L. E., "Concrete Waterproofing," 128 pp., Sir Isaac Pitman and Sons, London, 1947.

A general treatment of older methods. Many details on construction practice. Integral waterproofers and general coatings covered, but chief emphasis is on bituminous coatings.

65. Hunter, S. C., "Waterproofing with Emulsified Asphalt," Maint. Eng. 89, 432 (1931).

Properties of asphalt emulsions for waterproofing and application directions.

66. Llewellyn, H. M., "Waterproofers," Chem. and Ind. 1934, 929.

A review of dampproofers and waterproofers. Linseed oil and varnish were effective. Bituminous materials were the least.

67. Lord, E. C. E., "Effect of Tar, Ammonium Fluosilicate, and Sodium Hydroxide on Alkali-Resistance of Concrete," Public Roads 23, 282 (1944).

Concretes were treated and exposed to sulfate solutions. Water-gas tar was an effective waterproofer.

68. Nicholson, G. F., "Improved Asphalt Treatment for Concrete Piles in Sea Water," Eng. News Record 103, 95 (1929).

A description of the vacuum method of application used on piles in Los Angeles harbor.

Silicones

69. Anon., "State Testing Value of Silicones," Penn. Road Builder 29, No. 1, 9 (1956).

Describes a test application of 8 silicone materials to highway slabs on US 22 at Progress, Pa.

70. Bass, R. L. and Porter, M. R., "Silicones," in Moilliet, J. L., "Waterproofing and Water-Repellency," Chap. 5, 1963.

Preparation and structure of silicones, their water-repellency, and applications, including masonry.

71. Britton, H. B., "New York State's Experience in Use of Silicones," Highway Res. Board, Bull. 197, 13 (1958).

Describes field tests with water-base silicone on highway structures in New York state. Treatments resulted in lessened absorption and scaling and increased light reflectance.

72. Cahn, H. C., and Mackey, R. V. Jr., "Extending Concrete Highway Durability and Light Reflectance with Silicones," Am. Soc. Testing Materials, Bull. 235, 37 (Jan. 1959).

Laboratory and field tests showed the application of silicones to result in lowered absorption, increased scaling resistance, and increased light reflectance when wet.

73. Dolch, W. L., "Factors Affecting the Penetration by Water of Bituminous and Silicone Coatings," Proc. Am. Railway Eng. Assoc. 61, 195 (1959).

A laboratory study of the influence of accelerated weathering on the contact angle of water on bituminous emulsion and silicone films. The silicone films degraded on weathering. The contact angle of water on the filled bitumin films increased with weathering, possibly due to an increase in roughness.

74. Dolch, W. L., Unpublished Reports of Joint Highway Research Project, Purdue University, 1960.

Experimental treatments of highway bridges by both water- and solvent-base silicones. No difference has been noted between treated and untreated sections. The main failure has been popouts.

75. Grieb, W. E., "Silicones as Admixtures for Concrete," Highway Res. Record No. 18, 1 (1963).

Various types of silicones were tested as integral admixtures for concrete. Water-base silicones increased strength and durability. All silicones caused excessive retardation of set.

76. Hussell, D. J. T., "Freeze-Thaw and Scaling Tests on Silicone-Treated Concrete," Hwy. Res. Abstracts, Dec. 1962.

Two types of silicones were used to treat both air-entrained and non-air-entrained concrete. The treatment resulted in some benefit to the non-air-entrained concrete but none to that containing entrained air.

77. Hussell, D. J. T., "Freeze-Thaw and Scaling Tests on Silicone-Treated Concrete," Highway Res. Record No. 18, 13 (1963).

Laboratory tests showed little or no benefit effected by silicone treatments.

78. Kather, W. S. and Torkelson, A., "Sodium Methyl Siliconate. Nature and Applications," Ind. Eng. Chem. 46, 381 (1954).

Directions for preparation by hydrolysis of trichloromethylsilane. Material is a superior water repellent compared with wax emulsions and aluminum stearate. It can be used as an integral water repellent. Its alkalinity may cause staining if applied to some limestones.

79. Klieger, P. and Perenchio, W., "Silicone Influence on Concrete Resistance to Freeze-Thaw and De-Icer Drainage," Highway Res. Record No. 1[illegible], 3[illegible] (1[illegible]).

Various silicones applied to concrete were tested in the laboratory. Silicones were found to have no benefit or even to be detrimental. They reduced initial absorption, especially on vertical surfaces, but longer exposure resulted in the same absorptions as those of controls.

80. Lanning, F. C., "The Effectiveness of Silicones as Water Repellents When Applied to Various Types of Limestone," Kansas State Coll. [illegible], No. [illegible], [illegible] pp. (1[illegible]).

A study of the application of silicones to 6 different types of limestones. The water-base sodium methyl siliconate was effective but two solvent-base compositions were not. The effectiveness decreased after weathering.

81. Lanning, F. C., "Effectiveness of Silicones as Water Repellents When Applied to Concrete," Trans. Kansas Acad. Sci 61, 334 (1958).

Solvent and water-base silicones were applied to various types of concrete. The materials were effective generally but not on relatively porous, lightweight concrete.

82. Mardulier, F. J., "Scaling Resistance of Concrete Improved Through Silicones," Highway Res. Board, Bull. 197, 1 (1958).

A laboratory study and summary of field experience. A solvent-base silicone penetrated further into concrete than a water-base one. Penetration was influenced by type of finish. Scaling was materially reduced by silicone treatment.

83. Plungyanskaya, M. N. and Moskvin, V. M., "The Hydrophobization of Concrete with Organic Silico-Fluoride Compounds as a Method of Increasing its Resistivity," Beton i Zhelezobeton 1958, 218; C.A. 52, 1[illegible]072.

Recommends the use of sodium ethyl siliconate as an integral and surface waterproofer combined.

Epoxy and Related Coatings

84. ACI Committee 403, "Guide for Use of Epoxy Compounds with Concrete," Proc. Am. Concrete Inst. [illegible], 1121 (1962).

A guide to all aspects of use of epoxy compounds with concrete, including waterproofing. Methods of surface preparation are discussed, and a test for the bond strength of epoxy materials to concrete surfaces is given.

85. Affleck, J. G., "Waterproofing of Concrete or Masonry," U.S. Patent [illegible] (1[illegible]); C.A. [illegible], 1501[illegible].

Waterproofing is accomplished by impregnation of concrete surface with an acrylic compound and polymerization in-situ to an impermeable gel

86. Davis, H. E., "Epoxies Fight Acids-Protect Concrete and Steel," Plant Eng. 1[illegible], March, 1[illegible].

Describes the application and success of an epoxy application in a low pH environment.

87. James, J. G., "Use of Epoxy Resins in Road and Bridge Surfacing," Resin Rev. 1, No. 3, [illegible] (1961); Hwy. Res. Abst., Jan. 1962.

A general review of the application of epoxy resins to highway work and a description of experimental work at the Road Research Laboratory in England.

88. Lee, H. and Neville, K., "Epoxy Resins," McGraw-Hill, New York, 1957.

A monograph summary of all aspects of epoxy resins.

89. Mason, N. A., "Floors and Decks," Bldg. Res. Inst. (Natl. Acad. Div.) Pub. No. 563, 24 (1959).

A discussion of paints for concrete floors, especially the advantages of urethane coatings.

90. Pimbly, C. E., "Epoxy Resin Guards Powerful Nuclear Reactor," Res. and Develop. 13, No. 4, 54 (1962).

Describes an epoxy coating used on a reactor, including on concrete parts as a waterproofer.

91. Uraneck, E. A. and Sonnenfeld, R. J., "Resinous Waterproof Coatings for Plaster, Concrete, and the Like," U.S. Patent 2984857 (1959); C.A. 53, [illegible].

A waterproof coating is formed on masonry surfaces by application of a neutral or slightly acidic solution of a copolymer prepared from an acidic monomer and a conjugated diene. Reaction with multivalent metal ions of the base material forms an insoluble coating.

92. U. S. Army, Corps of Engineers, "Epoxy Resins for Use on Civil Works Projects," Tech. Rept. No. [illegible], U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., [illegible].

A summary with many details of Corps of Engineers and other experience. Coatings are included.

93. U. S. Bureau of Reclamation, "Epoxy Resins for Concrete Construction and Repair," U. S. Dept. of Interior, Bur. of Reclamation, General Rept. No. [illegible], [illegible] (1961).

A report of the Bureau's experience with epoxies in the concrete field. The page cited is a description of laboratory tests that showed thin epoxy coatings to greatly reduce damage of concrete from freezing and thawing.

Miscellaneous Coatings

94. Anon., "SBR Latex Improves Cement Mortars," Can. Chem. Processing 47, No. 1, 60 (1963).

Styrene-butadiene latexes incorporated in mortars give improved physical properties and resistance to chemical attack and freezing and thawing. Thin overlays of these mortars bond well to concrete and are being used for bridge deck resurfacing.

95. Krokosky, E. M. and Daouk, A. M., "Bridge-Deck Sealing and Organic Inhibitors," 41 pp., Massachusetts Inst. of Technology, 1963.

Synthetic-resin latexes were used as integral materials in relatively large proportions. Polyvinylidene chloride and polyvinyl acetate were effective in reducing scaling in laboratory tests.

96. Sneno, T. and Kinoshita, K., "Glossy Waterproof Coatings for Cement Products," Japan Patent 7435 (1959); C.A. 54, 50416.

A formulation for a covering of calcite and other materials. A mixture of Portland cement, kaolin, and cristobalite was mixed with a calcium chloride solution, and the resulting paste applied to concrete was then treated with moist carbon dioxide and cured in water. The resulting layer was glossy, hard, durable, and waterproof.

97. Yukara, S., "Polyethylene Water Repellents," Japan patent 1857 (19[illegible]); C.A. [illegible], [illegible].

A polyethylene gel was made by heating with spindle oil and cooling. When used on concrete this material gave a waterproof coating.